

~~CLAIMS~~a WHAT IS CLAIMED IS:

1. Manufacturing method for M type hexaferrite powders of formula  $A Fe_{12}O_{19}$  where A designates a metal chosen among Ba, Sr, Ca, Pb, or their mixture wherein:
  - a) an iron oxide  $Fe_2O_3$  and an A compound are provided, usually under the form of powders, and a mixture is made of said iron oxide and said A compound, with a molar ratio  $n = Fe_2O_3 / AO$ ,
  - b) said mixture is shaped in the form of agglomerates of shape and size adapted to the calcination stage, and these are calcinated in an oven, typically between  $1100^{\circ}C$  and  $1300^{\circ}C$ , in such a way as to form M type ferrite,
  - c) said calcinated agglomerates are ground to obtain a fine ferrite powder, characterised in that
    - at the previous stage a) of said calcination:
      - 1) said mixture is formed with a ratio n comprised between 5.7 and 6.1,
      - 2) simultaneously with the formation of said mixture or after this, said mixture is ground, so as to have both a mixture with a degree of homogeneity at least equal to a predetermined threshold, and an average particle size of predetermined value comprised between 0.25 and  $1 \mu m$ ,
      - 3) before or during said grinding, one introduces into said mixture an agent for controlling the microstructure (ACM),
      - at stage b), the calcination conditions together with the nature and content in ACM are chosen in order to obtain, at the end of the calcination phase, a ferrite

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material under the form of a porous cake presenting at the same time the following properties:

- \* a transformation yield in crystallised M ferrite greater than 95%,
- 5 \* an apparent density  $d_a$  lower than 3.5 and, preferably, lower than 3, or a porosity higher than 30% and preferably higher than 40%,
- \* low cohesion energy at the grain boundaries between primary particles leading to high brittleness, in order
- 10 to replace the grinding of stage c) by a simple dispersion of said cake.

2. Process according to claim 1 wherein, as ACM, one incorporates into said mixture an additive allowing the transport of  $Fe^{3+}$  in gaseous phase, during the

15 calcination phase, typically  $FeCl_3$ , typically with a content comprised between 0.1 and 0.5% by weight of mixture.

*Suba'* 3. Process according to one of the other of claims 1 and 2, wherein one incorporates into said mixture, as

20 ACM, and typically at a content comprised between 0.1 and 0.5% by weight of mixture, a volatile oxide capable of substituting for  $Fe_2O_3$  or A, during said calcination, typically  $Bi_2O_3$  or  $V_2O_5$ , the incorporation of said volatile oxide being compensated, in the case

25 of excess charge, by another addition of a bivalent metal substituting for  $Fe^{3+}$  to ensure the valency balance.

4. Process according to any one of claims 1 to 3 wherein said mixture is calcinated:

30 - either in two stages: at a temperature comprised between 1225°C and 1275°C for less than 5 minutes, then

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at a temperature comprised between 1100°C and 1150°C for at least 30 minutes,

- or in a single stage at a temperature comprised between 1200°C and 1300°C, for a time comprised between 30 and 90 minutes.

5           5. Process according to any one of claims 1 to 4 wherein said grinding is constituted of a dry grinding or comprises a humid phase grinding, the dry or humid grinding being carried out in the presence of metallic  
10 or ceramic grinding elements, typically bars or balls loaded with or constituted of  $ZrO_2$  or tungsten carbide WC, the low contents of Zr or W, typically between 0.05 and 0.5% by weight of said mixture, transferred by wear and rubbing of said bars or balls to said mixture, or  
15 added to said mixture, acting under finely dispersed form as ACM agent.

          6. Process according to any one of claims 1 to 4 wherein one provides an iron oxide  $Fe_2O_3$  with an average particle size comprised between 0.25 and 1  $\mu m$   
20 and in which one replaces said grinding of stage a), under 2), by a dry mixture or a dispersion in humid phase.

          7. Process according to any one of claims 1 to 6 wherein one furthermore incorporates into said mixture  
25 a particle size control agent, abbreviated as ACTP, typically silica, calcium oxide, a derivative of silica, or a combination of silica and calcium oxide, typically  $CaSiO_3$ , with a content in equivalent silica comprised between 0.1 and 1% by weight of said mixture.

30           8. Process according to any one of claims 1 to 7 wherein the ratio n is equal to  $6 \pm 0.1$ .

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9. Process according to any one of claims 1 to 7 wherein the ratio  $n$  is chosen equal to  $5.9 \pm 0.1$ .

10. Process according to any one of claims 1 to 7 wherein the ratio  $n$  is chosen equal to  $5.85 \pm 0.15$ .

5 11. Process according to any one of claims 1 to 10 wherein one incorporates into said mixture substitution trivalent products B for A, chosen among Bi, La and rare earths, typically under the form of oxides, and bivalent products C for  $\text{Fe}^{3+}$  substitution, chosen among  
10 Ni, Co, Mg, Cd, Cu, Zn, in such a way as to balance the valencies, with a content chosen to form ferrites of formula  $\text{A}_{1-x}\text{B}_x\text{C}_x\text{Fe}_{12-x}\text{O}_{19}$ , with  $x$  ranging between 0.05 and 0.45.

12. Hexaferrite cake having an apparent density  
15 lower than 3 and an average particle size comprised between 0.25 and  $1 \mu\text{m}$ , obtained by the process according to any one of claims 1 to 11, in which said dispersion is suppressed replacing said stage c) of grinding.

20 13. Hexaferrite fine powder obtained by dispersion of the cake of claim 12.

14. Magnets obtained from powder according to claim 13.

25 15. Magnetic recording media obtained from powder according to claim 13.

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